

PATENT SPECIFICATION.



Application Date : July 8, 1943. No. 11120/43.

579,246

Complete Specification Left : July 10, 1944.

Complete Specification Accepted : July 29, 1946.

PROVISIONAL SPECIFICATION

Improvements in the Production of Hydrogen.

We, BRITISH NON-FERROUS METALS RESEARCH ASSOCIATION, a corporation organised under the laws of Great Britain, of 81-91, Euston Street, London, N.W.1, ESTHER MYRIAM DORIS SMITH, WILLIAM ALBERT BAKER, and EDWIN ANDREW GUTHRIE LIDDIARD, all British Subjects, and all of the Association's address, do hereby declare the nature of this invention to be as follows:—

This invention relates to the production of hydrogen gas.

At the present time this gas is used in relatively large quantities in a large number of scattered sites many of which are remote and relatively inaccessible. On the other hand, no satisfactory methods exist at present for generating the hydrogen gas on the site where it is to be used and therefore the gas must be transported in heavy and expensive cylinders, with the result that heavy transport costs add to the cost of producing the hydrogen.

The object of the present invention is to obviate the above drawbacks and disadvantages, by providing simple and effective means for generating the gas on the site where it is to be employed (whether on land or at sea) although it will be understood that the process of our invention may be employed in any location where this procedure may seem desirable.

Our invention is based upon the observation that magnesium alloys which contain particles of more noble metals, corrode rapidly with the evolution of hydrogen when in contact with moisture and particularly with water or sodium chloride solution or sea water, but while the rate of reaction of such alloys with water is sufficient to cause rapid deterioration without special protection in most corrosive environments, nevertheless the rate of evolution of hydrogen is insufficient to make them generally interesting as potential sources of hydrogen gas.

We have found, however, that by increasing the proportions of such noble metals, for example, copper, nickel or iron, we can cause the rate of reaction

with water to be sufficiently rapid to provide a useful hydrogen generator and our invention therefore consists in a process for producing hydrogen, which comprises taking an alloy or mixture of magnesium and a more noble metal present in the alloy or mixture in substantial amount and bringing such alloy or mixture in contact with water which may, if necessary, be rendered conductive by the addition of a salt or salts in solution or otherwise.

Further features of the invention will be apparent from the description given hereafter.

In carrying our invention into effect in one convenient manner, we take magnesium in the form of powder and this we mix with iron filings or granulated, powdered, or reduced iron and we compress the mixture into a block or pellet of suitable size. The best proportions of magnesium and iron have not yet been determined accurately, but satisfactory results are obtainable when the iron is present in the proportion of from 3 to 40% of the mixture and very satisfactory results are obtained with about 20% of iron.

We find that when these pellets are exposed to the action of salt water the rate of the reaction may in some cases be such that gas equivalent to approximately 100 times the volume of the original pellet or block is evolved per minute. We have also found it of advantage to incorporate in the mixture a small proportion, for example, 5% of a soluble chloride, such for example, as ammonium chloride, as this increases the reaction rate somewhat and markedly increases the reactivity of the compressed mixture with relatively pure water. The total volume of gas which can be produced from this mixture approximates very closely to the theoretical volume, assuming complete reaction of the magnesium present in the mixture with the water, that is to say, a mixture containing 1 lb. of magnesium powder would produce approximately 400 litres or 14 cubic feet of hydrogen.

With the normal method of transporting hydrogen at the present time in cylinders, it is usually found that a cylinder

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AMENDMENT - SEE LAST PAGE

Price 25s.

Price 75p¹

capable of holding 150 cubic feet of hydrogen weighs approximately 120 lb. and it will be seen that by means of our invention 120 lb. of magnesium powder
 5 —iron powder mixture will produce approximately 1500 cubic feet of hydrogen, so that the advantage of our invention over the normal method as regards transport is approx-
 10 imately 10:1. The mixture can be transported to the site where it is desired to generate hydrogen and by allowing the mixture to come in contact with water, salt solution or sea water in a simple genera-
 15 tor, hydrogen can be very quickly and conveniently produced.

A suitable generator may be constructed on the lines of an acetylene generator or we may employ a cylinder or tube open
 20 at the bottom and having a controlled outlet at the top, with a grid, grating or construction at a convenient point in the length of the cylinder upon which the pellets or blocks of mixture may be
 25 placed. When the tube with the pellets therein is immersed in water, salt solution or sea water, hydrogen gas is immediately generated and may be led to the point at which it is to be used.

30 When no further gas is required, the outlet is closed, whereupon the pressure

within the tube rises and thus depresses the water below the level of the block or pellets so that generation of hydrogen ceases. So soon, however, as the outlet
 35 tap is again opened the water rises within the tube and gas generation is resumed.

It will be understood that the invention is not confined to the use of magnesium and iron powders nor to the proportions indicated above. Similar results
 40 may be obtained by incorporating copper or nickel with the magnesium powder or in cases where extremely rapid generation of hydrogen is not required satisfactory results may be obtained by the use
 45 of solid alloys not made from powders in which the noble metal is added by alloying. For example, moderate reaction rates with salt water have been obtained
 50 from alloys consisting of 15% copper and 85% magnesium or 20% nickel and 80% magnesium. It is not possible to alloy the iron with pure magnesium in sufficient quantities to prepare a satisfactory
 55 solid alloy, but by the introduction of a further alloying element, for example silicon, sufficient iron may be introduced into the alloy to cause a moderately rapid
 60 reaction.

Dated this 8th day of July, 1943.

MARKS & CLERK.

COMPLETE SPECIFICATION.

Improvements in the Production of Hydrogen.

We, BRITISH NON-FERROUS METALS RESEARCH ASSOCIATION, a corporation organised under the laws of Great Britain, of 81—91, Euston Street,
 65 London, N.W.1, ESTHER MYRIAM DORIS SMITH, WILLIAM ALBERT BAKER, and EDWIN ANDREW GUTHRIE LIDDIARD, all British Subjects, and all of the Association's address, do hereby declare the nature of this invention and in what
 70 manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the production of hydrogen gas.

At the present time this gas is used in relatively large quantities in a large number of scattered sites many of which are remote and relatively inaccessible, and it
 80 is usually necessary to transport the gas to the site in heavy and expensive cylinders with the result that heavy transport costs add to the cost of producing the hydrogen.

85 The object of the present invention is to obviate the above drawbacks and disadvantages by providing simple and effective

means for generating the gas on the site where it is to be employed (whether on land or at sea) although it will be
 90 understood that the process of our invention may be employed in any location where this procedure may seem desirable.

It has already been proposed to produce hydrogen by reacting on water with
 95 aluminium or magnesium admixed with one or more of the metals lead, tin and zinc, and no claim is made herein to such process.

Our invention is based upon the observation that magnesium alloys which contain particles of more noble metals, corrode rapidly with the evolution of hydrogen when in contact with moisture and particularly with water or sodium
 105 chloride solution or sea water, but while the rate of reaction of such alloys with water is sufficient to cause rapid deterioration without special protection in most corrosive environments nevertheless the
 110 rate of evolution of hydrogen is insufficient to make them generally interesting as potential sources of hydrogen gas.

We have found, however, that by

increasing the proportions of a more noble metal selected from the group consisting of iron, copper, or nickel, we can cause the rate of reaction with water to be sufficiently rapid to provide a useful hydrogen generator, and our invention therefore consists in a process of producing hydrogen which consists in alloying or mixing magnesium with a more noble metal selected from the group consisting of iron, copper or nickel or mixing magnesium with a salt or oxide of such metal, and bringing such alloy or mixture into contact with water which may, if desired, be rendered conductive, as by the addition of a salt or salts in solution.

The salt or oxide of the more noble metal must be such that when the mixture comes into contact with water or aqueous solution, the salt or oxide decomposes in contact with magnesium and provides by chemical replacement a finely divided deposit of the more noble metal on the magnesium particles. Examples of such more noble metal salts or oxides are copper sulphate, ferric oxide and ferric chloride. Thus we have found that if ferric oxide is mixed with magnesium powder and ammonium chloride the reaction proceeds at least as vigorously as if iron powder were used.

Further features of the invention will be apparent from the description given hereafter.

In carrying our invention into effect in one convenient manner we take magnesium alloy in the form of powder or finely divided swarf or turnings and mix this with iron oxide or iron in the form of filings or granulated powder or reduced or mechanically powdered iron of such a fineness to pass the 200 mesh of the British Standards sieve. We may also incorporate into the mixture about 5% of a soluble chloride such as ammonium chloride. We then compress the mixture into blocks or pellets of suitable size. The rate of reaction of the mixture when exposed to water will vary with the proportions of magnesium and iron or iron oxide and, while the iron content may vary from 1% to 40%, it is generally unnecessary to exceed an iron content of 30%. Satisfactory results are obtained with about 20% iron. The mixture when pressed into pellets should be stored in air- and moisture-tight containers since it will otherwise deteriorate on exposure to a moist atmosphere and generate hydrogen which may be a source of danger. For this reason it is an advantage if the constituents of the mixture including the soluble chloride are not markedly hygroscopic since the presence of hygroscopic substances in the mixture will increase

the liability to deteriorate on storing in moist atmospheres.

We find that when these pellets are exposed to the action of salt water the rate of the reaction may in some cases be such that gas equivalent to approximately 100 times the volume of the original pellet or block is evolved per minute. We have also found that the incorporation in the mixture of a small proportion, for example, 5% of a soluble chloride as indicated above, increases the reaction rate somewhat and markedly increases the reactivity of the compressed mixture with relatively pure water. The total volume of gas which can be produced from this mixture approximates very closely to the theoretical volume assuming complete reaction of the magnesium present in the mixture with the water, that is to say, a mixture containing 1 lb. of magnesium would produce approximately 400 litres or 14 cubic feet of hydrogen.

With the normal method of transporting hydrogen at the present time in cylinders, it is usually found that a cylinder capable of holding 150 cubic feet of hydrogen weighs approximately 120 lb. and it will be seen that by means of our invention 120 lb. of 80% magnesium powder—20% iron powder mixture will produce approximately 1350 cubic feet of hydrogen so that the advantage of our invention over the normal method as regards transport is approximately 9:1. The mixture can be transported to the site where it is desired to generate hydrogen and by allowing the mixture to come in contact with water, salt solution or sea water in a simple generator, hydrogen can be very quickly and conveniently produced.

A suitable generator may be constructed on the lines of an acetylene generator or we may employ a cylinder or tube open at the bottom and having a controlled outlet at the top with a grid, grating, or construction at a convenient point in the length of the cylinder upon which the pellets or blocks of mixture may be placed. When the tube with the pellets therein is immersed in water, salt solution or sea water, hydrogen gas is immediately generated and may be led to the point at which it is to be used.

When no further gas is required, the outlet is closed, whereupon the pressure within the tube rises and thus depresses the water below the level of the blocks or pellets so that generation of hydrogen ceases. So soon, however, as the outlet tap is again opened the water rises within the tube and gas generation is resumed.

It will be understood that the inven-

tion is not confined to the use of mixtures of magnesium and iron powders nor to the proportions indicated above. Similar results may be obtained by incorporating
 5 copper or nickel with the magnesium powder or in cases where extremely rapid generation of hydrogen is not required satisfactory results may be obtained by
 10 the use of solid alloys in which the noble metal is added by alloying instead of by the use of mixtures of comminuted metals as described above. For example, moderate reaction rates with salt water
 15 have been obtained from alloys consisting of 15% copper and 85% magnesium or 20% nickel and 80% magnesium. It is not possible to alloy pure magnesium with iron in sufficient quantities to prepare a satisfactory solid alloy, but by the
 20 introduction of a further alloying element, for example, silicon, sufficient iron may be introduced into the alloy to cause a moderately rapid reaction.

Having now particularly described and
 25 ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process of producing hydrogen
 30 which consists in alloying or mixing magnesium with a more noble metal selected from the group consisting of iron, copper or nickel, or mixing magnesium with a salt or oxide of such metal, and
 35 bringing such alloy or mixture into contact with water which may, if desired,

be rendered conductive as by the addition of a salt or salts in solution.

2. A process according to claim 1 in which the mixture consists of magnesium
 40 metal in comminuted form such as powder or turnings and the more noble metal also in finely divided form, the mixture being compressed or worked into pellets
 45 or other convenient form.

3. A process according to claim 1 in which the mixture consists of magnesium metal in comminuted form and a salt or oxide of the more noble metal.

4. A process according to claim 2 or 3
 50 in which the mixture also contains a soluble and preferably non-hygroscopic chloride.

5. As an article of manufacture, a mixture of finely divided magnesium, finely
 55 divided iron, and a soluble chloride, compressed or worked into pellets or other convenient form.

6. As an article of manufacture, a mixture of finely divided magnesium, ferric
 60 oxide, and a soluble chloride, compressed or worked into pellets or other convenient form.

7. Improved process for the production of hydrogen substantially as herein
 65 described.

8. Hydrogen gas, whenever produced by the processes claimed in claim 1-4 or claim 7.

Dated this 10th day of July, 1944.

MARKS & CLERK.

SPECIFICATION NO. 579,246

By a direction given under Section 17(1) of the Patents Act 1949 this application proceeded in the name of, British Non-Ferrous Metals Research Association, a British Company of 81-91, Euston Street, London, N.W.1.

THE PATENT OFFICE,
 1st March, 1950.

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